

Formation of cyanide bridged networks at the air/water interface

J. Culp, G. Weerasekera, D.R. Talham, and R. Duran
Chemistry Department, University of Florida, Gainesville, FL USA

Introduction

Supramolecular chemistry is a synthetic approach aimed at creating complex structures from relatively simple building blocks for potential use in nanoscale devices [1]. The method takes advantage of weak-to-moderate bonding interactions between complementary molecular components to create a structure that is greater than the sum of its parts. The intermolecular forces that have traditionally been employed are Van der Waals in nature and include pi-pi stacking, hydrogen bonding, and host-guest interactions. To expand the potential applications of supramolecular chemistry, we are investigating the combination of transition metal coordination geometries with an air/water interface as the architectural driving forces in the assembly of monolayer supramolecular square grid arrays.

Methods and Materials

The diffraction experiments were carried out at the Advanced Photon Source (APS) insertion device beamline 10-ID employing a double silicon monochromator, operated by MR-CAT. X-rays of energy 8050 eV were deflected onto the water surface at a critical angle of 1.8 mrad by a glass deflecting mirror coated with a platinum stripe. The Langmuir trough assembly was specially designed and constructed by KSV Instruments, Finland, to be housed inside an eight-circle Huber goniometer. The trough was mounted on MOD1 vibration isolation table, purchased from Hynlincs, Germany. The trough environment was kept under a helium purge to minimize radiation damage to the monolayer. Monolayers of 4-dioctaceylaminopyridinepentacyanoiron(III) (1) were spread on a 1 mM Ni(NO₃)₂ subphase from a dilute chloroform solution. The monolayer was compressed to a pressure of 1 mN/m. Diffraction over Kxy was monitored by a NaI scintillation counter and normalized to the incident beam intensity. Background scattering was reduced with xy and z soller slits mounted in front of the diffraction detector.

Results and Discussion

Figure 1 shows the two theta scan for a monolayer of (1) at 25° C at a surface pressure of 1 mN/m on a pure water subphase. The absence of any features indicates a lack of order for the monolayer over pure water. Conversely, when (1) is spread over a 1 mM nickel subphase and compressed to 1 mN/m at 25° C, two broad features centered at approximately 9 and 13 degrees in two theta are observed in the diffraction pattern shown in Figure 2. This result indicates that the nickel ions are forcing some order in the monolayer. Based on an expected iron cyanide nickel separation of 10 angstroms for a square grid arrangement, the (1,0) reflection should occur at approximately 9 degrees

in two theta and the (1,1) reflection at approximately 13 degrees. The width of the peaks in the diffraction pattern indicates a very low quality to the desired grid network. Further refinement of the assembly procedure and the amphiphilic building block are being investigated to further improve the film quality.

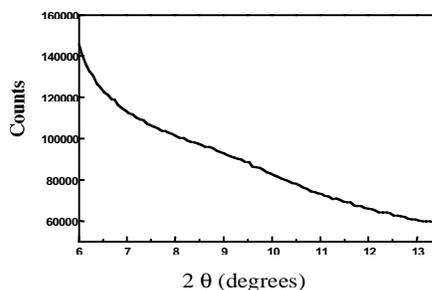


Figure 1: Grazing incidence x-ray diffraction (GIXD) pattern for a monolayer of (1) at 1 mN/m and 25° C over pure water.

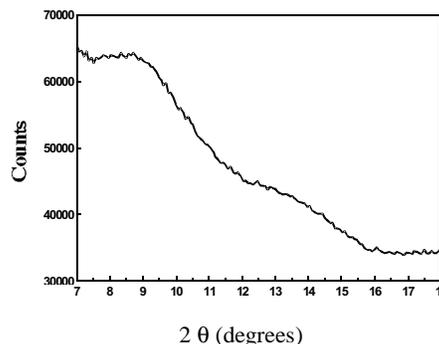


Figure 2: GIXD pattern for a film of (1) reacted on a 1 mM nickel subphase at 1 mN/m and 25° C.

Acknowledgments

Use of the APS was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38.

Reference

- [1] *Comprehensive Supramolecular Chemistry, Vols. 1-11* (Pergamon, Oxford, 1996).